SYNTHESIS AND CHARACTERIZATION OF A NEW BIMETALLIC CATALYST, GJL-46, AND ITS USE IN THE CATALYTIC HYDROSILYLATION OF PHENYLACETYLENE

By
Gabriel Joseph LaBonia

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Approved by

Advisor: Professor T. Keith Hollis

Reader: Professor Daniell Mattern

Reader: Professor Nathan Hammer
ABSTRACT

GABRIEL JOSEPH LABONIA: Synthesis and Characterization of a New Bimetallic Catalyst, GJL-46, and Its Use in the Catalytic Hydrosilylation of Phenylacetylene
(Under the direction of Professor T. Keith Hollis)

A new bimetallic catalyst was synthesized from the metalation of 1,1’-(1,3-phenylene) bis(4-butyl-1 H-1,2,4-triazol-4-iium) iodide with silver oxide and the transmetalation of that complex with Rh(COD)₂OTf. The structure of the compound, GJL-46, with molecular formula C₃₄H₄₆I₂N₆Rh₂, was confirmed with mass spectra analysis, ¹H NMR and ¹³C NMR. The catalytic activity of the produced molecule, GJL-46, with molecular formula C₃₄H₄₆I₂N₆Rh₂, in the hydrosilylation of phenylacetylene is reported.

Ph SiMe₂Ph

GJL-46

Ph ≡ ≡ + PhMe₂SiH

Cat

Ph SiMe₂Ph
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INTRODUCTION

Carbenes

The first evidence of the existence of carbenes and their structure was set forth by Buchner, Curtius, Staudinger, and Kupfer between the years of 1885 and 1912.\textsuperscript{1,2} Following the discovery of carbenes and the ensuing years, it was believed that these molecules were too unstable to be isolated and that they only existed as short-lived intermediates. However, in 1964, the first transition-metal carbene complexes were isolated by the work of Fischer and Maasbol.\textsuperscript{3} This work led to Fischer receiving the Nobel Prize in 1973.\textsuperscript{4} Since Fischer’s discovery of these complexes, their chemistry has been explored for both organic synthesis and catalytic processes.\textsuperscript{5}

Carbenes are a class of molecules that contain divalent carbon atoms. These molecules are a neutral and highly reactive species. Their high reactivity comes from the electron deficiency in their outer electron shell, which contains a pair of unpaired valence electrons.\textsuperscript{6} The general structure of a carbene is shown above in Figure 1.

![General Carbene Structure](image)

Figure 1. General Carbene Structure.
Free carbenes have two distinct spin states. The two spin state are singlet and triplet as shown in Figure 2. In the singlet state, both electrons are paired in the same sp^2 orbital, leaving the p orbital unoccupied. Triplet state carbenes contain one electron in both the sp^2 and p orbitals and are generally of lower energy than singlet state carbenes.7 Carbenes in the singlet state tend to have reactive properties, whereas triplet state carbenes tend to exhibit interactive properties.8 Substituent function groups on the carbene can also control the proportion of triplet-to-singlet states of the system.9

![Singlet State](image1.png) ![Triplet State](image2.png)

**Figure 2.** Spin states of carbenes. This figure illustrates the two possible spin configurations of carbenes. The singlet state, with paired electrons in one orbital, is generally of higher energy than the triplet state that has two unpaired electrons in different orbitals.

Classic reactivity for carbenes includes insertion and addition reactions. Both of these reactions can occur inter- or intra- molecularly.10 Carbenes can be used in insertion reactions between C-H bonds, C-O bonds, C-N bonds, C-X bonds, and also N-H bonds. Carbenes used in addition reactions usually produce alkenes and cyclopropanes as shown in Figure 3. Cyclopropane rings are very difficult to produce due to their instability and high ring strain. Carbenes work for this process due to their high reactivity.
Stable Carbenes

Carbenes were used in chemistry far before they were individually isolated and these highly reactive species were first isolated in 1988 by Guy Bertrand. The carbenes he created contained P and Si. These (phosphino)(silyl)carbenes have been dubbed “push-pull carbenes” due to the ability of substituents with opposing electronneutrality to stabilize the singlet carbenes.\textsuperscript{11} The push-pull carbenes discovered to date have very different reactivities. These (phosphino)(silyl)carbenes react with electrophilic alkenes but are fairly resistant to binding metals.\textsuperscript{12} Push-pull carbenes and push-push carbenes, such as N-Heterocyclic Carbenes, have not been reported for reactions such as cyclopropanations but will readily bind with metals. This activity of diamino carbenes is due to their nucleophilicity and low electrophilicity.\textsuperscript{13}

Figure 3. Two examples of original carbene reactivity. This figure illustrates two of the main reactions of carbenes. The reaction on the top is a simple insertion reaction. On the bottom is a simple cyclopropanation reaction.
**N-Heterocyclic Carbenes**

N-Heterocyclic Carbenes are the specific class of carbenes explored in this research. N-Heterocyclic Carbenes (NHC’s) are carbenes stabilized by two nitrogen atoms that are part of the same ring structure. As previously discussed, these NHC’s will readily react with transition metals. The first NHC metal complexes were simultaneously reported in 1968 by Ofele, Wanzlick and Schonherr.\(^\text{14,15}\) For this reason, there was not a good synthetic method for their synthesis until Arduengo provided a good method in 1991.\(^\text{16}\) Now, NHC’s can be synthesized in large quantities, which was vital to this research.

The first crystalline NHC was synthesized and characterized in 1990 by Arduengo, Harlow, and Kline. This molecule utilized imidazole as the N-heterocyclic precursor. The carbene, which was only stable in the absence of oxygen and moisture, formed colorless crystals and demonstrated kinetic and thermodynamic stability.\(^\text{17}\) NHC’s can also be derived from other molecules, such as pyrazolium and triazolium. This research eventuated the use of triazole as the source for the N-heterocyclic carbene complex.

**Catalysis**

A catalyst is a substance that increases the rate of a chemical reaction without being consumed or changed during the chemical reaction. A catalyst speeds up the rate of reaction by lowering the activation energy, which is the minimum energy barrier for a chemical reaction to occur. This process can be outlined and illustrated in a reaction coordinate diagram; a two dimensional graph with energy on the Y-axis and reaction
progress on the X-axis. The beginning point on the diagram is the current energy of the reactants and the final point on the diagram is the energy of the products. In order to move forward to the products, a higher energy transition state must be overcome. This high energy transition state corresponds to the activation energy of the reaction. At this transition state there is enough energy in the system for current bonds to break and new bonds to form. This transition state is the rate-limiting portion of the reaction and determines how fast or slow a reaction will occur. The lower the energy of the transition state, the faster a reaction will proceed.

With this in mind, one way to increase the rate of a reaction is by lowering the energy of the transition state. This change is effected by a catalysis. As shown in Figure 4, the catalyzed reaction has a lower energy gap between the reactants and the transition state. Catalysis is relevant to this research in that the created molecule serves as a catalyst for hydrosilylation reactions.
Figure 4. Reaction Coordinate Diagram. This diagram illustrates the change in activation energy for a catalyzed versus uncatalyzed reaction.

**Thermal vs. Kinetic Product**

When two possible products can be produced from a reaction depending on reaction condition, the reaction is said to be under thermodynamic control or kinetic control. The kinetic product is formed more quickly but has a product with a lower stability and thus a higher energy level, whereas the thermodynamic product is of lower energy and thus higher stability. The kinetic product is so called because it is formed faster than the thermodynamic product due to its lower activation energy. This concept is illustrated in the reaction coordinate diagram in Figure 5.
Figure 5. Reaction Coordinate of Kinetic and Thermodynamic Product. This figure illustrates the reaction coordinate diagram for the kinetic and thermodynamic product of a reaction.

Generally the thermodynamic product dominates when the reaction is allowed to occur for a longer period of time. The thermodynamic product dominated because it is the energetically more stable product and will form when the reaction has additional time to come to equilibrium. Higher temperatures facilitate this equilibrium by adding more energy to the reaction and cause more of the thermodynamic product to form.18
METHODS

Synthesis and Characterization of A New Bimetallic Complex

The first reaction in the four step process is the synthesis of 1,3-di(1 H-1,2,4-triazol-1-yl)benzene from 1,3-dibromobenzene and 2.5 equivalents of 1,2,4-triazole. The reaction equation is shown in Figure 6. A list of reagents, reaction conditions, and results from both trials can be found in Table 1(1-3) and Table 2(1-3).

The second reaction is the synthesis of 1,1’-(1,3-phenylene)bis(4-butyl-1,2,4-triazol-4-iium) iodide from the 1,3-di(1 H-1,2,4-triazol-1-yl)benzene (Figure 6) and 1-iodobutane. The reaction equation is shown in Figure 7. A list of reagents, reaction conditions, and results can be found in Table 3(1-3).

The third reaction is the synthesis of bis(u-1,3-bis(4’-butyl-1’,2’,4’-triol-2’-ylidene)benzene-κ-C)tetra-μ³-iodotetrasilver(I) from 1,1’-(1,3-phenylene)bis(4-butyl-1,2,4-triazol-4-iium) iodide (Figure 7), silver oxide, and potassium hydroxide. The reaction equation is shown in Figure 8. A list of reagents, reaction conditions, and results can be found in Table 4(1-3).

The final reaction is the synthesis of GJL-46 from bis(u-1,3-bis(4’-butyl-1’,2’,4’-triol-2’-ylidene)benzene-κ-C)tetra-μ³-iodotetrasilver(I) and [Rh(COD)₂OTf]. The reaction equation is shown in Figure 9. A list of reagents, reaction conditions, and results can be found in Table 5(1-3).
Figure 6. Reaction of Synthesis of 1,3-di(1H-1,2,4-triazol-1-yl)benzene (GJL-28 & GJL-29).
1,2,4-Triazole and copper oxide were added to a 250mL round bottom flask with a stir bar. 90 mL of dimethylsulfoxide(DMSO), potassium carbonate, and 1,3-dibromobenzene were added to the reaction flask. The reaction was left, stirring, for 48 hours in a 150 °C oil bath. When the reaction time was complete, the reaction mixture was dissolved in 900mL of dichloromethane, DCM. A Buchner filter funnel, with a medium frit, was packed with 2 layers of Celite®(SiO₂) and 60 grams of alumina(Al₂O₃). The reaction mixture, dissolved in DCM, was poured through the filter, which was under vacuum. The solid remaining in the filter frit was washed with a 10:1 DCM:IPA solution. The solution that went through the filter was concentrated under reduced pressure, and the remaining solids were left under high vacuum overnight. The remaining dry product was weighed and stored.
1,2,4-Triazole and copper oxide were added to a 250 mL round bottom flask with a stir bar. 90 mL of DMSO, potassium carbonate, and 1,3-dibromobenzene were added to the reaction flask. The reaction was left, stirring, for 48 hours in a 150 °C oil bath. When the reaction time was complete, the reaction mixture was dissolved in 900 mL of dichloromethane. A Buchner filter funnel, with a medium frit, was packed with 2 layers of Celite and 60 grams of alumina(Al₂O₃). The reaction mixture, dissolved in DCM, was poured through the filter, which was under vacuum. The solid remaining in the filter frit was washed with a 10:1 DCM:IPA solution. The filtrate was concentrated under reduced pressure and the remaining solids were left under high vacuum overnight. The remaining dry product was weighed and stored.
Figure 7. Reaction of synthesis of 1,1′-(1,3-phenylene)bis(4-butyl-1H-1,2,4-triazol-4-ium) iodide (GJL-34).
First, a 250 mL schlenk flask was covered in foil. 3.2 grams of 1,3-di(1,2,4-triazol-1-yl)benzene and 22 mL 1-Iodobutane were added to a 250mL schlenk flask with a stir bar and 150 mL of Acetonitrile. The reaction was left, stirring, for 24 hours in a 150 °C oil bath. The reaction mixture was poured through a Buchner funnel with a medium frit. The solid remaining in the filter frit was washed with 20 mL of DCM. The remaining product was a pale yellow solid.
Figure 8. Reaction of synthesis of bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-iodotetrasilver(I).
First, a round bottom flask was covered in foil. 0.888 grams of 1,1’-(1,3-phenylene)bis(4-butyl-1,2,4-triazol-4-ium) was combined with 0.204 g of silver oxide, 0.088 g of potassium hydroxide and 40 mL of acetonitrile. The reaction was left, stirring, for 24 hours at room temperature. The solid remaining after filtration was washed with 10 mL of acetonitrile, 5 mL of methanol, and 2 washes of 20mL or diethyl ether. The remaining product was dried under reduced pressure leaving an off-white solid.
Figure 9. Synthesis of GJL-46.
First, 50 mg of bis(u-1,3-bis(4’-butyl-1’,2’,4’-triol-2’-ylidene)benzene-κ-C)tetra-μ³-iodotetrasilver(I), 58.8 mg of [Rh(COD)₂OTf], and 45.2 mg of NBu₄I were added to 10 mL of THF in a 50 mL round bottom flask. The reaction was stirred for 16 hours at room temperature. The reaction mixture was filtered and the volatiles were removed under reduced pressure to yield a yellow solid.
RESULTS AND DISCUSSION

The synthesis of GJL-46 was confirmed with ESI-Q-TOF Mass Spectrometry, $^1$H NMR and $^{13}$C NMR. The instrument used was a Waters SYNAPT ESI-QTOF and analysis was done in positive mode. The molecular ion peak, which should have been observed at 999 m/z, was not present in the mass spectra. This peak was not observed due to fragmentation of the molecular ion. The identifying peaks observed were for the molecular ion minus 1 Iodine and plus 1 Hydrogen(M-I+H). These peaks occurred around 873 m/z. A comparison of the isotopic resolution and experimental mass spectra is illustrated in Figure 10.

Most elements exist in nature as a mixture of isotopes, which are species that have the same number of electrons and protons but differ in the number of neutrons. This difference in the number of neutrons gives rise to some elements existing as different masses. The isotopic distribution in the figure takes into account the relative abundance of each isotope of the elements present in GJL-46. The highest peak in figure 10 corresponds to the mass at which each of elements exists as their most abundant isotope.
Hydrosilylation

In general, a hydrosilylation reaction involves adding a silica-hydrogen bond across an unsaturated carbon-carbon bond. This process of hydrosilylation is an effective way for the generation of a variety of silane complexes. In particular, hydrosilylation of alkynes offers a simple and direct means of producing vinylsilanes. In hydrosilylation reactions with the addition of silanes to terminal alkynes, three main isomeric vinyl silanes; α, β-E(trans), and β-Z(cis) can form. The general structures of these isomers are shown below in Figure 11.
The GJL-46 complex generated was expected to have catalytic activity in hydrosilylation reactions. The generated catalyst was used in the reaction of phenylacetylene with dimethylphenylsilane. This reaction illustrating three expected products (α, β-E(trans), β-Z(cis)) is shown below in Figure 12. This reaction was performed in an NMR tube at room temperature, and the reaction was monitored via $^1$H NMR spectroscopy, and the results are summarized in Table 6.

Figure 11. General isomeric structures of α, β-E(trans), and β-Z(cis).

Figure 12. Catalytic hydrosilylation of phenylacetylene and dimethylphenylsilane.
Table 6. Results for Catalytic Hydrosilylation of Phenylacetylene with GJL-46a

<table>
<thead>
<tr>
<th>Time</th>
<th>Conversion (%)b</th>
<th>αc</th>
<th>β-Zc</th>
<th>β-Ec</th>
</tr>
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<tbody>
<tr>
<td>5 min</td>
<td>24</td>
<td>1</td>
<td>98</td>
<td>1</td>
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<td>10 min</td>
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<td>15 min</td>
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<td>95 min</td>
<td>83</td>
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<td>97</td>
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<td>160 min</td>
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<tr>
<td>20 h</td>
<td>100</td>
<td>2</td>
<td>95</td>
<td>3</td>
</tr>
</tbody>
</table>

aGeneral conditions: GJL-46 complex (0.00359 mmol), dimethylphenylsilane (0.077 mL, 0.50 mmol), phenylacetylene (0.051 mL, 0.46 mmol), C6D6 (1 mL). bConversion determined by 1H NMR spectroscopy. cProduct ratios with respect to each other as determined by 1H NMR spectroscopy

A comparison of the catalytic activity of GJL-46 with other catalysts is shown in Table 7. As seen in the table, GJL-46 shows slightly better selectivity for the β-Z isomer than the three previously reported catalysts shown in the table. The third catalyst listed is very similar to GJL-46 with the difference coming in the use of imidazolium instead of triazolium. This complex showed was not as selective for β-Z isomer as well, but was run at a higher temperature (80 °C). This increase in temperature most likely led to more of the thermodynamic product being formed. The lack of β-Z product formed
with the first catalyst is consistent with the theory that the more stable product will be formed if energy or heat is added to the reaction.
Table 7. Comparison of GJL-46 Rhodium Complex with Some Previously Reported Hydrosilylation Catalysts

<table>
<thead>
<tr>
<th>Catalyst (mol %)</th>
<th>Substrate (mmol)</th>
<th>Conv (%)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>α</th>
<th>β-Z</th>
<th>β-E</th>
</tr>
</thead>
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<td><img src="2.4" alt="Image" />(^23)</td>
<td>0.46</td>
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<td>1.5</td>
<td>51</td>
<td>0</td>
<td>49</td>
</tr>
<tr>
<td><img src="0.78" alt="Image" />(^24)</td>
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<td>83</td>
<td>rt</td>
<td>24</td>
<td>3</td>
<td>91</td>
<td>6</td>
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<tr>
<td><img src="2-3.5" alt="Image" />(^24)</td>
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<td>99</td>
<td>rt</td>
<td>2.6</td>
<td>1</td>
<td>97</td>
<td>2</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The new compound synthesized, as illustrated in this thesis, shows catalytic activity for the hydrosilylation of phenylacetylene. The structure of the synthesized compound, GJL-46, was confirmed with ESI-Q-TOF Mass Spectrometry, $^1$H NMR and $^{13}$C NMR. This catalyst proved effective for the production of the $\beta$-Z isomeric vinylsilane in the reaction of phenyacetylene and dimethylphenylsilane. Vinylsilanes are useful as synthetic intermediates in organic synthesis due to their versatility and low toxicity. GJL-46 was compared to other previously synthesized catalysts and showed better selectivity for the $\beta$-Z isomer than a similar catalyst with the reaction run at room temperature.
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**GJL-46 ESI-MS**

Chemical Formula: \( \text{C}_26\text{H}_{32}\text{N}_6\text{Rh}_2 \)
Molecular Weight: 634.40

Chemical Formula: \( \text{C}_{18}\text{H}_{25}\text{IN}_6\text{Rh}_2 \)
Molecular Weight: 658.16
Dimethylphenylsilane

Phenylacetylene
GJL-46 Catalytic Study

5 Minutes

25 Minutes